

STRUCTURE DETERMINATION OF  
ALPHA-PINENE DIMERS

By

ALAN C. STACHOWICZ

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## INTRODUCTION

Alpha-pinene is one of the most abundant and readily available monoterpenes. Its properties and reactions have been studied extensively from both the theoretical and practical points of view [1]. The formation of camphene and bornyl chloride from  $\alpha$ -pinene were among the first reactions in retrosynthetic analysis [2]. The elucidation of its structure by degradation methods is one of the most elegant works in the history of structural organic chemistry.

Camphene, camphor, borneol alcohols, bornyl chloride, limonene and, recently,  $\beta$ -pinene are among the compounds produced from  $\alpha$ -pinene. Until several years ago it was one of the most important industrial solvents. Today it cannot compete with the much lower priced petrochemical solvents. This has brought up the need for new extensive study of the  $\alpha$ -pinene chemistry and development of new compounds and specialty products. There would be the outlet for the large natural supply of this material.

## EXPERIMENTAL

Treatment of  $\alpha$ -pinene with acids produces, in general, mixtures of monoterpenes, diene and alcohols. The diene are viscous liquids boiling at 353-358° C. They have been



known for more than one hundred years. However, because of the complexity of the dimeric structures and the difficulty of their separation and handling, very little has been done towards their systematic study and characterization.

Deville (3), in 1843, treated  $\alpha$ -pinene with sulfuric acid to produce a dimeric product. Since then, there have been reported dimerizations of  $\alpha$ -pinene with a large number of catalysts. These acidic catalysts can be divided into the following categories: (a) protic acids and inorganic acids, (b) Lewis acids and (c) alays and other metal oxides.

The earlier work on dimerization has been reviewed by Kozlovsk and Sapozhnik (4) and Delee (5). In Table I are summarized the most representative results.

In most of the earlier work either there is no attempt to find the structure of dimers or the structures proposed are purely speculative. The dimeric fraction is, in general, studied as one pure compound and so, the physical and chemical properties are average properties of the mixture of dimers.

Criss (6) and earlier workers have made the hypothesis that the dimers have the phenanthrene skeleton. Miller and Sapozhnik (7) isolated small amounts of phenanthrene derivatives by vigorous dehydrogenation of dimers with

TABLE 1

Polyethylene,  $\Delta E_{\text{max}} = 23.9 \text{ kcal/mole}$ 

Substrate	Percent H <sub>2</sub> O in solvent	$\eta_{\text{sp}}/\text{c}$ , dl./g.	$\eta_{\text{sp}}/\text{c}$ , dl./g.	$\eta_{\text{sp}}^0$	Remarks	Ref.
$\text{C}_2\text{F}_6$	40-45	0	1.70-1.73	0.915	70-100 $\text{C}_2\text{F}_6$ at 0°	12
$\text{C}_2\text{F}_6$		0	1.64-1.77	0.97	70% $\text{C}_2\text{F}_6$ in solvent	17
$\text{C}_2\text{F}_6$	50	0	1.75-1.79	0.915	conv. $\text{C}_2\text{F}_6$ 65-70°	16
$\text{C}_2\text{F}_6$	75	0	1.77-1.79	0.915	$\gamma\text{C}_2\text{F}_6$	7
$\text{C}_2\text{F}_6$	10	0.3	1.70-1.73	0.905	totally polymer	46
$\text{C}_2\text{F}_6$	50		1.65-1.71	0.905		8
$\text{BF}_3$	70	1	1.77-1.79	0.907	S.A. 16.06	46
$\text{BF}_3$	55-65		1.67-1.77	0.903	S.A. 16.13	46
CS <sub>2</sub>	10		3.06-3.10	0.94	1.905	19

sulfur. These are probably secondary reaction products and are not of much value as structural evidence.

Kendall and Ingold (4b) proposed structure I for the acid dissociation product. They proposed a mechanism of initial formation of tertiary esters which attack  $\alpha$ -pinene molecule to give the dimer.



I

Edson (5) studied the chemical properties and the Raman spectrum of the dimeric fraction from the treatment of  $\alpha$ -pinene with sulfuric acid. He recognized it as a mixture of mono and disulfide. He proposed the structures II and III.



II



III

The bromination and iodination experiments indicated more than one but less than two double bonds. However the molecular refraction was found 87.75 (calculated for two double bonds 87.87). This evaluation of molecular refraction could be explained by conjugation of the double bonds, but this is not possible in the structures he proposed.

Bohrer and Day [8] have proposed that dimerization of  $\alpha$ -pinene involves a hydrogen transfer and that the dimer is formed without isomerization. IV is proposed as one of the possible structures. This structure is not supported by any chemical or spectral evidence.



IV

Structure I + IV do not explain the fact that the dimeric alcohols formed in all these cases are optically inactive. The study of acid rearrangement reactions of  $\alpha$ -pinene indicates that the epoxidation ring opens very easily to form monocyclic or five member ring bicyclic ketones. So, it is very hard to believe that the dimer, which originates from the same carbonium ions as the monomers, contains epoxidation rings.

Kocher [9] has proposed the structure V. This structure is rather improbable considering the small amount of accumulation of dimer with S or Pd/S. The compound V would give aromatic compounds very easily.



V

Burles and Lather (14) were the first who isolated a pure dimer and studied its structure spectroscopically. The dimer studied was one of the main dimeric components of the reaction of  $\alpha$ -pinene with phosphoric acid. The proposed structure (VI) is consistent with most of the spectral data.



VI

The compound resisted hydrogenation indicating that the double bonds are highly hindered. The mechanism proposed for the formation of VI involves an intermediate terpenyl cation which attacks another  $\alpha$ -pinene molecule to form a terpenylterpenyl cation. The last ion, by equilibration and loss of a proton, gives VI. Molecular models indicate that VI is a strain free molecule.

#### Isomerization of $\alpha$ -pinene

It is obvious that the acid catalyzed isomerization of  $\alpha$ -pinene involves  $C_{10}$  carbenium ion intermediates which attack another  $\alpha$ -pinene molecule to give  $C_{20}$  carbenium ion intermediates. The  $C_{20}$  carbenium ions rearrange and finally lose a proton to give  $C_{20}H_{32}$  dimers.

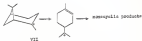
However, the  $\text{C}_{10}$  carbonium ions can lose a proton to give nonaromatic rearrangement products or are attacked by a nucleophile to give the corresponding compounds.

Because the dimeric and monomeric products have the same carbonium ion precursors,<sup>9</sup> it is reasonable to assume that a study of the nonaromatic fraction formed during an acid catalyzed reaction of  $\alpha$ -pinene will give clues to the structure and the mechanism of formation of the more complicated dimeric mixtures. This is supported by our observation that the number of dimeric products in a reaction mixture is proportional to the number of nonaromatic by-products. For these reasons it is considered useful to make a short review of the acid rearrangements of  $\alpha$ -pinene.

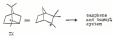
In general it is assumed that  $\alpha$ -pinene is attacked by a proton to give the carbonium ion VII. This rearranges in either of the schemes 1-3.

<sup>9</sup>For confirmation that there is mechanistic relationship between the monomeric and dimeric products of an acid catalyzed reaction of  $\alpha$ -pinene is supported by the data on the phosphoric acid catalyzed reaction. In this case the only monomeric products are generated from the tertiary carbon (see Table I). Structural studies on one of the main dimers formed in this reaction indicate that it has the same reactive intermediate (10).

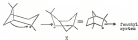
Scheme 1.



Scheme 2.



Scheme 4.



The rearrangement of VII to VIII and I could be considered unfavorable because we go from a tertiary to secondary carbocation ion. However by going from VII to VIII and I the space is relieved from the strain due to the cyclobutane ring.

It also states the experimental results are better explained by introducing non classical ions as intermediates or transition states (11). As early as 1938, Ingold (12 a,b) proposed the ion IX as intermediate in the con-  
 phase hydrochloride-iodoacetyl rearrangement.



IX

Similarly, the initial carbocation ion derived by protonation of toluene can be formulated as XII. This type of non classical bridged carbocation ion has been proposed in many other cases (13). Is by (13 a) found that mechanism of epichlorohydrin-4-epichlorohydrin rearrange involves the intermediate bridged cation XIII.



XII



XIII



The bridged cations XII and XIII can also be regarded as composites of the following resonance forms:



In the case of XIII the resonance form XIII a is not favored, and so, most of the catalytic product is the bicyclic compound. This is because the charge in XIII a is on a primary carbon atom. On the other hand, XII a is exceptionally favored as having the charge on a tertiary carbon atom.

Unfortunately there are no experimental data for cases where both the bicyclic and open chain ions have the charge on secondary carbon atoms. Such a system would be the catalyze of XIV, XV or XVI. In this case both the bicyclic and open-chain ions would be equally favored on terms of electronic charge distribution, and the decisive factor for their relative stability would be the steric interactions.



The non classical formulations, while not uniquely required by any specific result, most simply take account of products and reactivities (13-15). In spite of the fact that the classical ions can be intermediates in many instances, we shall use in the present treatment only classical formulations. The reason is that the classical ions can explain equally well our experimental results. On the other hand our experiments do not provide any conclusive evidence for the existence of non classical ions.

In general, the treatment of epoxides with an acidic catalyst yields a mixture of nonclassical rearrangement products. However it may occur the latter predominates, its nature depending upon the catalyst and the experimental conditions.

In Table I are summarized the results of the treatment of  $\alpha$ -pinene with various catalysts, in terms of the products formed.

The circumstantial data on this topic are collected over a long period of time, and they have been reported

TABLE 2

## DATA FROM REPRODUCED PRODUCTS OF A. FLORIDA

Reagent	Reactions Products	Reaction	Yield
$H_2SO_4$	n-terphenyl	In eq. mixture of chloroform	22
$H_2SO_4$	Monomers, diphenyls, terphenyls, terphenyl monomers	90% in water	20
$H_2SO_4$	terphenyl methyl ether	$H_2SO_4$ in acetone	15
$H_2SO_4$	diphenyls (100), terphenyls (100)	40-70% in water	26
$H_2SO_4$	p-terphenyl, naphthalene, o-terphenyl, 2,4-diphenyls, pyrene, 2,4,6-triphenyls	80% in water	10
none	Monomers, diphenyls, terphenyls, terphenyls, terphenyl monomers		25
$CH_3COOH$	diphenyls with some terphenyls	Same with acetone	26
acetic acid	terphenyl monomers with some diphenyls		15
phenol	naphthalene		24, 27
acetic acid	Monomers with some terphenyl monomers	In presence of acetone	15
acetic acid	terphenyl alcohol, terphenyl		24

Alcohol	Sub. Produced	Reaction	Ref.
1-ol, III (O-Cl, IV, 1)	isopropyl halide	in non polar solvents	1
PCl <sub>3</sub>	p-cresol		2
PCl <sub>3</sub>	p-cresol and others of chlorinated (isopropyl chlorides)		3
POCl <sub>3</sub>	chlorination (isopropyl chlorides)		2
SOCl <sub>2</sub>	isopropyl chlorides, isopropyl		17
Reimer-Tiemann	isopropyl	isopropyl reacts with isobutene, and isopropyl chloride	18
Cl <sub>2</sub>	isopropyl 4,4 - prop		19, 20
SO <sub>2</sub> in acid	hydrocarbons (SO <sub>2</sub> ), isopropyl, isobutene and p-cresol, isopropyl at isobutene, isopropyl, isobutene		21, 22
SO <sub>2</sub> in acid	hydrocarbons (SO <sub>2</sub> ), isopropyl, isobutene, isopropyl at isobutene, isopropyl, isobutene		23
SO <sub>2</sub> in -OH	hydrocarbons (SO <sub>2</sub> ), isopropyl, isobutene, isopropyl at isobutene, isopropyl, isobutene		24
SO <sub>2</sub> in H <sub>2</sub> O	isopropyl		25

by a large number of authors who, in some instances, contradict each other. So, it is not very easy to rationalize the relation between the type of catalyst and the type of predominating products. It would be very interesting to have the experimental results of a systematic study in this field. Votruba, Baron and Garber (14) proposed a mechanism to account for the formation of naphene as the chief product under conditions of heterogeneous acid catalysis. It is based on the preferential orientation of  $\alpha$ -pinene on the surface of the catalyst. The catalyst surface interacts with  $\alpha$ -pinene from the less hindered side (scheme 4). As a proton from the surface approaches

Scheme 4:



the 3-position, a second hydrogen atom is eliminated from the 1-position. Interaction of the catalytic surface with  $\alpha$ -pinene from the more hindered side will give limonene as a product. It must be noticed here that vapor phase isomerization of  $\alpha$ -pinene on silica yields dipentene as the major product. However in this case it is not clear whether the mechanism is a free radical or an ionic one.

Barwick and Papoula [15] have studied the reaction of aromatic organic acids with  $\alpha$ -pinene to give bornene esters. They have found that the best yields in bornene (88-93%) are obtained when the ionization constant of acids are between  $3.7 \times 10^{-4}$  and  $8 \times 10^{-6}$ . On the other side the formation of bornene is inhibited by the addition of an oxide (peroxide). In this last Serfaty likewise is found in very good yields.

If viewing the existing data we have been able to make the following generalizations:

a. The carbocation system is favored when the active ions are transition metal halides,  $BF_3$  in others, dry hydrogen halides in non polar solvents, aromatic acids, and phenols.

b. The mesoionic compounds are favored with organic inorganic acids, aromatic acids in the presence of fluorine acid, aliphatic acids, and  $BF_3$  in protic solvents.

It is of interest to notice that in the first class the catalytic conditions are such that the carbocation ions will not be free but they will be in the form of ion pairs or complexes. In, the charge is stabilized over the whole complex or ion pair. This would mean that the position of the charge on a secondary or tertiary carbon would not make such difference in the relative energies of the carbonium ions in terms of electronic distribution, and that steric factors would dominate.

The energy state of catalytic conditions would permit carbonium ions to be more free and so, the position of the charge in the ion would be the dominating energy factor. Thus the tertiary carbonium ion is favored over the secondary benzylic ions.

The above rationalization is of course purely speculative and we need a lot of experimental evidence before arriving at final conclusions.

### Summary of Project Goals

The main objectives of the present work were the following:

- a. Study the reaction of  $\alpha$ -pinene with boron tri-fluoride and find the best experimental conditions for the best yields in dimer.
- b. Find catalytic system that would give single dimeric structures with as few components as possible, and isolate the main components.
- c. Derive the structure(s) of the main dimeric components by studying their physical and chemical properties.
- d. Propose reasonable mechanism explaining the formation of the above dimer.
- e. Develop new synthetic routes to  $C_{20}$  compounds of relatively established structure which would be used as standards for the study of the properties and structure of dimers formed by acid dimerization of  $\alpha$ -pinene.

## REACTION OF $\alpha$ -PINENE WITH $\text{BF}_3$

### Discussion

To our knowledge, there is no systematic study of the reaction of  $\alpha$ -pinene with boron trifluoride.

Boron trifluoride ethereal reacts with alcohols in ether solutions to give esters (14). In protic solvents like alcohols and phenols the reaction products are mainly linear and terminal ethers and esters (15). The cyclic isoprenoids have not been studied in either case.

We have preferred boron trifluoride as ether Lewis acid catalyst because it is easier to handle and can be easily removed or recovered from the reaction mixture (16). On the other hand, it showed, under certain conditions, specificity in  $\alpha$ -pinene rearrangement reactions. This led us to believe that it could give simpler reaction mixtures.

Our expectations did not prove to be correct. The reaction of  $\alpha$ -pinene with  $\text{BF}_3$  gas was not selective and both the aromatic and aliphatic fractions were very complicated, as discussed in the next section.

The next step was either to use milder Lewis acids or modify the reactivity of  $\text{BF}_3$  by using it in the form



of coordination compounds. We have decided to follow this second approach<sup>10</sup>.

The catalytic activity of  $\text{BF}_3$  when used in the form of coordination compounds can be regulated by the equilibria  $\text{R}_2\text{O} + \text{BF}_3$ :



where  $(\text{base})_1$  is the base with which  $\text{BF}_3$  is coordinated and  $(\text{base})_2$  another reacting species.

The stronger the base or the larger its concentration, the more the equilibrium is driven to the left and the wider the action of  $\text{BF}_3$ .

We started using boron trifluoride ethers as catalysts. The results were about the same as in the case of  $\text{BF}_3$  gas. Large excess of ether did not help because the yields in dimeric compounds were very low and the main product was amorphous.

The next oxygenated base used was tetrahydrofuran which gives a stronger coordination compound due to reduced steric interactions (16). This catalyst gave higher reaction and there were fewer reaction products formed.

<sup>10</sup>Since it has been found that  $\text{SnCl}_4$  a Lewis catalyst milder than  $\text{BF}_3$  gives much cleaner dimeric alcohols than  $\text{BF}_3$  and is stronger under study (22).

However, the olefinic mixture was still composed of several isomers. We turned to nitrogen bases such as pyridine and triethylamine, to find that the coordination complexes were so strong that they did not react at all with  $\alpha$ -pinene.

The last group of bases tested was a series of chlorophosphines. These phosphines are written below in order of increasing basicity:



Phosphorous trichloride is such a weak base that it is very improbable that it can form any coordination compounds with  $BF_3$  under the reaction conditions. It did not dissolve ethyl ether from  $BF_3 \cdot C_2H_5O$ . The coordination compounds with the last two bases reacted extremely slowly yielding only a small amount of palpestric material.

Triethylphosphine gave a complex which reacted slowly to give such olefinic isomers and olefinic mixtures. When this olefinic mixture was treated with  $BF_3 \cdot C_2H_5O$  it gave a complex mixture having a T.P.S. pattern similar to that formed by the direct treatment of  $\alpha$ -pinene with  $BF_3 \cdot C_2H_5O$ .

### Catalytic action of $BF_3$

One very important factor involved in Lewis acid catalysis is the effect of small amounts of other compounds on the catalytic action of Lewis acids [27].

It has been demonstrated by Evans, Palanyi and co-workers [34] that polymerization of isobutene by boron trifluoride does not take place in the absence of traces of water or other proton-releasing substances. It was noted that by mixing  $\text{BF}_3$  with isobutene there was no color formed. The introduction of water vapor caused the formation of colored Lewis species.

Similar results were reported by Clark [35] for the reaction between styrene and  $\text{BF}_3$ . In dealing with the isomerization and dimerization mechanisms we will assume that  $\text{BF}_3$ , in presence of traces of water, acts in the following way:



The termination reaction will be



We have assumed that by the addition of  $\text{BF}_3$  to  $\alpha$ -pinene or isobutene of  $\alpha$ -pinene in polar solvents a bright red precipitate is formed. This is typical of the carbonium ion pairs formed whenever Lewis catalysts are involved [36]. Similar intensely colored precipitates are formed when  $\alpha$ -pinene is treated with  $\text{AlCl}_3$  or  $\text{TiCl}_4$  [35]. No intense color or precipitate is observed with mineral acid catalysts.

Therefore, we assume that the intermediate carbocation ions, formed during the Lewis acid catalyzed isomerization and distribution of  $\alpha$ -pinene, are in the form of ion pairs.

#### Reaction of $\alpha$ -pinene with $\text{BF}_3$ and $\text{BF}_3 \cdot \text{THF}$

In order to obtain the best yields of dieneic materials we have worked out the reaction of  $\alpha$ -pinene with  $\text{BF}_3$  or  $\text{BF}_3 \cdot \text{THF}$  under various experimental conditions. The results are summarized in Table 3.

The yields of diene were 18-82%. It was found that there is an optimum reaction time. By prolonging the reaction time there is an increase in polymers and decrease in diene. Similar observations were made for the phosphoric acid catalyzed reaction (43). In all cases the monomeric and dieneic fractions were complex and the various components appeared in about the same ratio.

The volatile fraction was composed of six or seven isomers. The main isomers were camphene and  $\beta$ -pinene, but there were also identified small amounts of limonene,  $\alpha$ -terpinene and  $\gamma$ -terpinene.

The dieneic fraction consisted of 18-19 components. Three of them make up the 68 per cent of the total mixture. The main component (XVII a) was usually found in amounts ranging from 15 to 35 per cent. The dieneic mixture obtained by method C was richer in XVII a. A typical gas chromatogram of a dieneic mixture is given in Figure 3.

TABLE 3

Composition of solution with known  $\alpha$ -phs solids

Method	Dis- solv.	Time min.	Amount of precip. g./100	Amount solid g./100	Yield solid g./100
1. Addn. of $Mg \cdot m_2O$ to $\alpha$ -phs	100	2	1	20	50-55
2. Addn. of $\alpha$ -phs to $Mg \cdot m_2O$	70	2	1	20	50-55
3. Addn. of $Mg$ to $\alpha$ -phs	70	3	—	2	20
4. Addn. of $Mg$ to $\alpha$ -phs	100	2	—	2	40
5. Addn. of $Mg \cdot m_2O$ to $\alpha$ -phs	40	15	5-10	16	61



Figure 1. Total ion chromatogram of the diethyl esters from the oxidation of propene with  $\text{O}_3$  in dichloro methane.

The solid residue was a heavy brown to dark brown material with green fluorescence. Its molecular weight was 450-580, which corresponds to a mixture of telomers and heteromers.

Both the dimeric and the polymeric mixtures absorbed strongly in the ultraviolet region from 230 to 300 m $\mu$ , with maxima at 253 and 297 m $\mu$ . Their infrared spectra indicated highly substituted and vinyl double bonds. After hydrogenation with Pd/C catalyst the UV and IR absorption due to unsaturation disappeared, and there was a decrease in refractive index. The dimeric mixture had no optical activity.

Small amounts of pure dimers IVIIa and IVIIb were isolated by preparative gas chromatography. Dimer IVIIa had an absorption maximum at 253 m $\mu$  (ca.10,000). The infrared spectrum indicated trisubstituted double bonds and vinyl groups. The mass spectrum had different peaks at  $m/e$  43, 55, 69, 81, 91, 104, 130, 169, and 190 (molecular ion), and two small peaks at 274 and 380. There is at present no satisfactory explanation for the existence of the last two peaks in the mass spectrum. Dimer IVIIb had very similar spectral characteristics. Both dimers were optically inactive.

#### Reaction of monomers with $BF_3$ in tetrahydrofuran

As discussed earlier, a number of coordination compounds of  $BF_3$  were used as catalysts in the place of  $BF_3$

as  $\text{BF}_3 \cdot \text{C}_2\text{H}_5\text{O}$ . 75% conversion compounds were formed by mixing equimolecular amounts of  $\text{BF}_3 \cdot \text{C}_2\text{H}_5\text{O}$  and the corresponding olefin.

The composition of the dimeric mixture formed from the reaction of  $\alpha$ -pinene with the triethylphosphorus complex, depended on the reaction conditions. Under the conditions described in the experimental part, the mixture contained five main components. The yield of isomer VIIIa was better than in any other previous method of dimerization (Figure 1).

In another experiment it was attempted to study the variation of the composition of the monomeric and dimeric reaction mixture as a function of time (Figures 3 and 4). The conclusion from this experiment is that dimer VIIIa is probably not a direct reaction product but is formed as a product of rearrangement of another dimer, later change under the reaction conditions. Another conclusion is that  $\beta$ -caryophyllene, which is among the main monomeric by-products, is formed through  $\gamma$ -terpinene, probably by air oxidation.

#### Reaction of $\alpha$ -pinene with other $\text{BF}_3$ complexes

The reaction of  $\text{BF}_3$  complexes with various and tri-alkylphosphines with  $\alpha$ -pinene gave unreacted starting material. The complex with diphenyldichlorophosphine gave a small amount of fluorescent polymeric material but the rest was unreacted  $\alpha$ -pinene.





Figure 2. Superimposed chromatograms of the diastere esters from the reaction of *n*-glucose with D, L, and DL tartaric acids (from left to right).

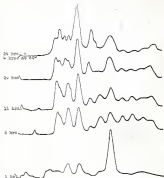


Figure 3. Effect of the reaction time on the composition of the diacetic mixture from the reaction of 4-pyrene with  $\text{BF}_3$  in tetrahydrofuran.

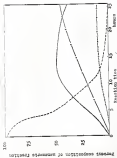


Figure 6. Variation of the composition of the various fractions from the reaction of 4-phenyl-2,3,5-trimethyl-1,4-dioxane with tetrahydrofuran: 1. Tetrahydrofuran, 2. Tetrahydrofuran + tetrahydrofuran, 3. Tetrahydrofuran + tetrahydrofuran + tetrahydrofuran, 4. Tetrahydrofuran + tetrahydrofuran + tetrahydrofuran + tetrahydrofuran, 5. Tetrahydrofuran + tetrahydrofuran + tetrahydrofuran + tetrahydrofuran + tetrahydrofuran.

The reaction of  $\alpha$ -pinene with  $\text{BF}_3 \cdot \text{OEt}_2$  at  $15-25^\circ \text{C}$ . produced a diastere mixture with two main components (Figure 1). The reaction was mild and relatively slow. The yields were low and not very reproducible but in general they depended upon the amount of the complex added. Prolonged reaction times did not improve the yields.

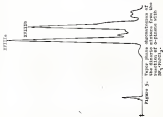
The temperature was always kept below  $25^\circ \text{C}$ . otherwise the reaction became fast and the products resembled those formed from the reaction of  $\text{BF}_3$  and  $\alpha$ -pinene. The reaction was carried out in excess  $\alpha$ -pinene or in benzene with the same results.

The molecular fraction was composed of unreacted  $\alpha$ -pinene, camphene and some  $\beta$ -pinene.

The two main diastere (XXIII and XXIV) were separated by preparative gas chromatography. We attempted to separate them with liquid partition chromatography on a silica gel column but without success, mainly because they were adsorbed on the column. Such inseparability was not observed when diastere from  $\text{BF}_3$  catalyzed dimerization were passed through a silica gel column.

It is interesting to notice that the diastere XXIII and XXIV, unlike the diastere formed by all other methods, possess optical activity.

The retention times of XXIII and XXIV in V.G.C. fall in the same range with those of diastere formed by  $\text{BF}_3$ .



initiation. Incidentally, XVIIa and XVIIb have the same retention times. However, they have different spectral properties.

When XVIIa and XVIIb were treated with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  they gave a mixture of dimers having a T.G.C. pattern very similar to that of the dimer mixture formed by dimerization of  $\alpha$ -pinene with  $\text{BF}_3$  (Figure 5). It is reasonable to assume that the dimers XVIIa and XVIIb are precursors of many of the dimers formed by treating  $\alpha$ -pinene with  $\text{BF}_3$  gas or  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ .

### DISCUSSION<sup>1</sup>

#### Analyses

Gas chromatographic analyses were performed with F and F 780 or Aerograph 85-FL-608, both with flame detection. The following columns were used: FFAP 80%  $14'/1/8"$ , 60'/ $1/8"$ , and 10'/ $1/8"$ , SE 30 100', 5'/ $3/8"$ ; Apiezon L 140'  $1/8'/1/8"$ , Carbowax 100 100', 15'/ $1/8"$ ; Tenaxsil 900, 15'/ $1/8"$ . The solid support in all cases was Chromosorb P 80/100. Preparative gas chromatography was performed with an Avian prep 1-750 with thermal conductivity detector. The best preparative column was found to be FFAP 30% on Chromosorb P, 17'/ $3/8"$ .

<sup>1</sup>The authors wish to thank Dr. Mary Orr, Mrs. Lee Macgregor-Lynn, Dr. John Polgottier, Dr. D. D. Davis, Dr. R. D. Hughes and Dr. G. Buchanan for obtaining most of the experimental data.

Nuclear magnetic resonance spectra were determined with a Varian DP-60 High Resolution Nuclear Magnetic Resonance spectrometer, in carbon tetrachloride solution or neat, with tetramethylsilane as internal standard.

Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer or Beckman DU 1B spectrophotometer.

Ultraviolet spectra were recorded with a Bausch and Lomb Spectronic DU spectrophotometer in hexane or ethanol solutions.

Optical rotations were measured with a Rudolph polarimeter in one decimeter chloroform.

Elemental weights were obtained either by mass spectroscopy or on a Beckman DU 400 Vapor Pressure Osmometer.

Mass spectral data were obtained on a DuPont 4140-GF-4000, Model 2B-107, mass spectrometer.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tennessee.

Fractional distillations were carried out with a Kistler-Peart spinning band column (25 theoretical plates).

### Materials

Alpha-pinene and all other terpenes were donated by Clifton Company (Jacksonville, Florida);  $\alpha$ -pinene [b.p.  $155^{\circ}$ ,  $[\alpha]_D^{25}$   $19.8^{\circ}$ ,  $n_D^{25}$  1.4621]; (+)- $\alpha$ -pinene ( $[\alpha]_D^{25}$   $+43.5^{\circ}$ ); (-)- $\alpha$ -pinene ( $[\alpha]_D^{25}$   $-43.8^{\circ}$ ).

Sodium hydroxide solution was, freshly distilled, Easton Kodak, pure grade. Monophosphines were donated by Victor Chemical Works and trialkylphosphines by Gerliche Chemical Works, Inc. Sodium hydroxide was obtained from Ketal Hydroides, Inc. Nitrobenzene (anhyd.) was distilled over sodium. Alkylenes and alkanes were obtained from Perkinelmer Chemicals, Inc. and Columbia Organic Chemicals Co., Inc. and were used without further purification; Isobutylbenzene was obtained from Phillips Petroleum Company. The U. S. I. I. Kaeli Shores Laboratories supplied us with a series of n-alkanes which were used as standards for gas chromatographic analysis.

#### Reaction with $\text{BF}_3$ and $\text{BF}_3 \cdot \text{OEt}_2$

Method A: 1.5 ml.  $\text{BF}_3 \cdot \text{OEt}_2$  was added dropwise at room temperature to 136 g. n-pentane. The temperature rose slowly to  $45^\circ$  and then very fast to  $160^\circ$ . After stirring for 1.5 hours the mixture was washed with dilute ammonia and water and dried over 5 g.  $\text{CaH}_2$ .

In another run,  $\text{BF}_3 \cdot \text{OEt}_2$ , 1.5 ml., was added to n-pentane, 36 g., precooled to  $-34^\circ$  C. with dry ice. A bright orange solid precipitated out. At about  $-15^\circ$  C. the solid changed to a brown syrup. There was no apparent reaction until the temperature rose to  $25^\circ$  C. At this point the reaction became vigorous as above.



Reflux 3 (inverse addition): To 1 ml. of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ , 1.6 g. of  $\alpha$ -pinene were added with stirring and heating in an ice bath. The temperature was maintained at  $33-35^\circ$  during the addition. After stirring for one hour, the mixture was worked up as above.

Reflux 4: To 51.6 g. of  $\alpha$ -pinene, cooled in an ice bath, gaseous  $\text{BF}_3$  was passed for one hour with vigorous stirring. A brown syrup precipitated out but the reaction was very slow until the ice bath was removed.

Reflux 5: To 66.1 ml. of  $\alpha$ -pinene, gaseous  $\text{BF}_3$  was passed for 0.5 hour with stirring. Stirring was continued for another half hour and the reaction mixture was treated as before.

Reflux 6: To 133 ml. of  $\alpha$ -pinene in 250 ml. benzene were added 13 ml.  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . The mixture was stirred at room temperature for 15 hours.

#### Epimerization with $\text{BF}_3$ in tetrahydrofuran

a. To 30 ml. tetrahydrofuran and 20 ml.  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ , cooled in ice-water, were added 180 ml.  $\alpha$ -pinene. After stirring for 2 hours at  $0^\circ \text{C}$ ., and for 15 hours without cooling, the mixture was worked up as above.

b. To 100 ml.  $\alpha$ -pinene, cooled in an ice bath, was added at once 25 ml.  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  in 40 ml. tetrahydrofuran. Samples were taken every hour and were quenched by shaking with 10% ammonia. The reaction temperature was  $15^\circ \text{C}$ .

from the 6th to 12th hour,  $10^{\circ}$  C. from 12d to 14th hour,  $20^{\circ}$  C. from 14th to 24th hour, and  $45^{\circ}$  C. from 24th to 30th hour.

#### Gas chromatographic analysis

The volatile fractions were analyzed by a Carbowax 20M column, temp.  $100^{\circ}$  C., flow 30 ml./min. The diene fractions were analyzed by Carbowax 20M, Tenaxid 100 and STW columns, at  $100-120^{\circ}$  C. with flow rates of 50-100 ml./min.

The molecular weight of the diene mixtures was determined by mass spectroscopy and with a vapor pressure osmometer and was found to be 278, corresponding to  $C_{12}H_{22}$ . The optical rotation (found  $[\alpha]_D^{25} = 0$ ) was measured in carbon tetrachloride solution.

#### Reaction with $BF_3 \cdot OEt_2$

The reagent was formed by mixing equimolecular quantities of  $BF_3Cl_2$  and  $BF_3 \cdot Et_2O$ . To 100 ml.  $\alpha$ -pinene (b.p.  $135^{\circ}$ ,  $[\alpha]_D^{25} = +10.9^{\circ}$ ), kept at  $10-20^{\circ}$  C. was added, slowly and with good stirring, 8.66 mole (120 g.)  $BF_3 \cdot OEt_2$ . The two phase system was stirred for three hours at  $20^{\circ}$  C. The reaction mixture was poured into a flask containing crushed ice and was shaken for 0.5 hour. To the mixture was added more ice and 10 ml. 30% ammonia, and the shaking continued for another 0.5 hour. The organic phase was separated and washed with 3 x 10 ml. 10%  $Na_2CO_3$ , 3 x 10 ml.

150 g<sub>2</sub>A<sub>2</sub>, 2 x 10 ml. 10% NaCl, and 2 x 10 ml. saturated sodium chloride solution, and dried over  $\text{CaH}_2$ . It was distilled through a short column to give 12 grams of a monomeric fraction, 12 grams of dimeric material and 7 grams of a polymeric residue.

The two main components of the dimeric mixture were isolated by preparative gas chromatography. (75% 140 column, helium gas 150 ml./min., temp. 200° C.)

XVIII:  $[\alpha]_D^{25} -21.9^\circ$  (10% in  $\text{CCl}_4$ ),  $n_D^{25} = 1.4507$

XVIII:  $[\alpha]_D^{25} +8.7$  (10.4% in  $\text{CCl}_4$ ),  $n_D^{25} = 1.4505$

Both spectra of both compounds have the narrow peak at 373 and no peaks above 370.

#### Elemental analysis:

Calculated for $\text{C}_{20}\text{H}_{32}\text{O}_2$ :	C, 84.11	H, 11.40
Found for XVIIIa:	C, 84.22	H, 11.70
Found for XVIIIb:	C, 84.46	H, 11.81

The dimeric mixture (II 62a) was fractionated with a spinning band column into four fractions. The first fraction (II 64a) contained about 75 per cent XVIIIa and the third fraction (II 64c) contained about 75 per cent XVIIIb. These enriched fractions as well as the original dimeric mixture were used for hydrogenation, dehydrogenation and condensation experiments.

### Hydrogenation of Diene

Various diene fractions were hydrogenated in 10% or 40% with 5% palladium on charcoal at atmospheric pressure and room temperature. Hydrogen uptake was not reproducible varying from 1.3 to 1.6 equivalents of hydrogen. In Table 4 are given the refractive indices of a number of diene fractions before and after hydrogenation.

The hydrogenated products did not absorb at about 330  $\mu$  in the UV region and there was no diene absorption in the infrared spectra.

TABLE 4

### Refractive Indices of Diene Before and After Hydrogenation

Fraction	$n_D^{20}$ Before Hydrogenation	$n_D^{20}$ After Hydrogenation
Diene mixture (Fig. 5)	1.5118	1.5008
II 44a (75% IVIIIa)	1.5110	1.4978
II 44c (75% IVIIIa)	1.5187	1.4978
1,3 <sup>a</sup> -diene	1.4938-1.5032	No change

### Hydrogenation of Diene

The diene fractions were heated with equal amounts of 5% palladium on charcoal for 24 hours at 240° C. under nitrogen. The mixture was extracted with benzene and the

regions separated in space. The changes in refractive index are tabulated in Table 5.

TABLE 5  
Refractive Indices of Glass  
Before and After Dehydrogenation

Fraction	$n_D^{20}$ Before Dehydrogenation	$n_D^{20}$ After Dehydrogenation
	Before Dehydrogenation	After Dehydrogenation
II 6A	1.5110	1.5085
II 6B	1.5127	1.5097
Mixture of diphenols	1.5030	1.5030
70% 2,2,4,4	1.5112	1.5096

The IR spectra of dehydrogenation mixtures indicated the existence of phenyl group absorption at 1500 and 1600  $\text{cm}^{-1}$ . The mass spectrum had peaks at 270 and 266 but also a very high peak at 124 and diffused peaks between 180 and 200. In the n.m.r. spectrum of the dehydrogenated mixture (II 6A), the ratio of aromatic protons to all others was 1:14. The small amount of aromatic protons and the mass spectral data indicate first, that the mixture contains five member ring bispheno units<sup>4</sup> and only one six member

<sup>4</sup> Dehydrogenation made by Schuler (12) showed that even at above 500° C. it is very difficult to dehydrogenate phenols and impossible to dehydrogenate monosubstituted compounds containing five member rings (fenchone, camphene, bornylene).

Fig. 200d. That, during the reaction, disproportionation takes place. This disproportionation is very common in cyclobutane systems [41]. The late peak at 4.19% of the mass spectrum corresponds to compound(s) formed by such hydrogen disproportionation.

### Analysis of the diacetic mixture [21.5%]

The diacetic mixture was obtained in  $\text{CH}_2\text{Cl}_2$  solution. The oxoacids formed were decomposed with hydrogen peroxide.

The volatile fraction was neutralized with solid sodium carbonate then distilled with a spinning band column. The first fraction had a peak, in T.P.C., corresponding to acetone. It gave a precipitate with 2,4-dinitrophenylhydrazine and positive iodoform test. The solid residue was acidified with dilute sulfuric acid. The acidic solution had an odor characteristic to formic acid, reduced ammoniacal silver nitrate solution, and gave negative phenylhydrazine and 2,4-dinitro tests.

The non volatile fraction was a mixture of keto acids. It was soluble in alkaline solution and reprecipitated by acidification with dilute hydrochloric acid. It gave a positive iodoform test. With 2,4-dinitrophenylhydrazine it gave red phenylhydrazones. Treatment with diazomethane in ether produced keto esters. Reduction of the keto esters with sodium borohydride gave hydroxy esters.

TABLE I

Characteristic Infrared Absorptions of the Insoluble  
Residue, Before and After Hydrolysis

	Characteristic Infrared Absorptions ( $\text{cm}^{-1}$ )
Insoluble residue (non volatile fraction)	3400-3300 (broad), 1767, 1710 (sharp)
Residue with $\text{H}_2\text{O}$	1775
Residue with $\text{CH}_3\text{CO}_2$	1770, 1767
Residue with diethyl- phosphorotriacetate	1765, 1705 (sharp, overlapping)

## STRUCTURES OF DIMERS XVIIIa AND XVIIIb

Spectroscopic data, hydrogenation, dehydrogenation and chemical experiments support the following structures for the dimers, XVIIIa and XVIIIb, formed as main products of the reaction of  $\alpha$ -pinene with  $\text{BF}_3 \cdot \text{TiCl}_4$ .



XVIIIa



XVIIIb

The type of monomeric by-products formed during the reaction indicates that both monomers and dimers have the same reactive intermediates.

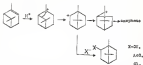
### Monomeric by-products

The main monomeric by-product (other than unreacted  $\alpha$ -pinene) is camphene. Camphene is always the major, or one of the major, products when  $\alpha$ -pinene is treated with  $\text{BF}_3$  under various conditions.

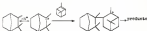
When  $\text{BF}_3$  (or  $\text{BF}_3 \cdot \text{TiCl}_4$ ) reacts with neat  $\alpha$ -pinene or with solutions of  $\alpha$ -pinene in hydrocarbon the main monomeric products are camphene,  $\beta$ -pinene, and several other terpenes in smaller amounts.



When  $\text{BF}_3$  reacts with  $\alpha$ -pinene in ether, camphene is formed in yields up to 70% (32). In presence of acetic acid, isomeric or homol acetate (33) are formed. The formation of both camphene and the acetate esters involve the same carbocation like intermediates.



It would be reasonable to expect that the camphenyl cation formed, attacks another molecule of  $\alpha$ -pinene, instead of being deprotonated, and forms dimeric compounds:



#### Mass spectral data

Compounds  $\text{BFIBis}$  and  $\text{BFIBis}$  have very similar mass spectra (Figures 7 and 8). The base peak in both compounds

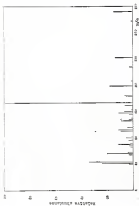


Figure 7. Mass spectrum of linear DNTDA

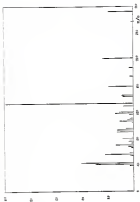
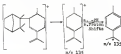


Figure 3. Base spectrum of linear MTHN.

is  $m/e$  133. This indicates that the molecule breaks very easily in the middle, and that the two monoterpenic units, comprising the dimer, are connected with a very weak bond. This bond must be through at least one tertiary carbon atom. No similar fragmentation was observed in the case of 1,3<sup>d</sup>-diisoprene (see next chapter), where the two monomeric units were connected through secondary carbon atoms.

After this first fragmentation, the two fragments later prefer to split to form the stable fragment  $m/e$  133, e.g.,



When the mass spectrum of monoterpene terpenes is taken at temperatures above 100° C., this kind of fragmentation ( $\Delta^{\circ} = 2$ ) is very common (83).

The ratio of peaks  $\frac{m/e\ 133}{m/e\ 135}$  is smaller in XVIIa than in XVIIb (Table 7), indicating that the breaking of the bond connecting the two units is easier in XVIIa. For similar carbon skeletons this bond would be broken easier if it were in an allylic position. This is the situation for dimer XVIIb.

TABLE 7

Relative Intensities of Major Fragments  
in the Mass Spectra of XVIIa and XVIIb





100 $\frac{I_{m/z}}{I_{47}}$	XVIIa	XVIIb
278	4.32	4.38
282	4.35	6.32
160	5.55	5.40
155	31.4	25.40
69	2.85	3.48
43	18.78	19.78
41	7.42	7.80

The ratio  $\frac{I_{278} + I_{282}}{I_{43} + I_{41}}$  is larger for XVIIb than for XVIIa. In Table 8 are given the values of this ratio for the two diastere and also for a number of monoterpenes. It is clear from this table that the diastere follow the same trend as the monoterpenes, although the mechanism of formation of these two fragments is not clear.

The fact that we get very small m/e 204 peaks in both compounds indicates that the bond connecting the two monoterpenic units is much weaker than the bond connecting the isopropenyl group to the six member ring. This indicates that the isopropenyl group is not in allylic position.

TABLE 8

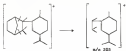
Ratio  $\frac{A^{\text{H}}(4)}{A^{\text{H}}(5)}$  for a Number of Terphenes<sup>(a)</sup>

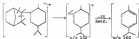
Compound	XTTIs	XTTIs				
$\frac{A^{\text{H}}(4)}{A^{\text{H}}(5)}$	0.51	0.36	4.00	7.37	1.30	3.30

<sup>(a)</sup> The values for numbers are computed from data in reference (44).

Monoterphenes having double bonds at 4, 7 or 7, 8 positions give much weaker  $A^{\text{H}}(4)$  peaks than other monoterphenes with similar carbon skeleton but with the double bonds in other positions. In Table 8 is given the relative height of the  $A^{\text{H}}(4)$  peak in a series of monoterphenes. The table was computed from data reported in reference 44.

The generation of the fragments 102 and 148 can be explained by the following fragmentation reactions:








The driving forces for the simultaneous breaking of two bonds are the steric relief and the formation of stable t-butyl or allyl carbocation ions.

TABLE 9

Relative Height of  $\delta^+$ -45 and  $\delta^+$ -43 Peaks  
in the Mass Spectra of  $\alpha$ -Tert-butyl Cyclohexadienes

Compound	$\delta^+$ -45	$\delta^+$ -43
	100	99
	100	73
	100	80
	39	(base peak $\delta^+$ -77)

TABLE 5 (continued)

Compound	$\delta^{\text{H}}-12$	$\delta^{\text{H}}-43$
	28	180
	5	100
	11	100
	5	100
	46	(broad peak $\delta^{\text{H}}=33$ )
	43	(broad peak $\delta^{\text{H}}=33$ )



The peak  $m/e$  69 which corresponds to the cyclopentadienyl cation indicates that in both molecules a bicyclic unit is present. Massella notes, citing that XIX, could be XX and XXI.



There is no case in the literature where the cyclopentadiene ring remained unaffected after the treatment of  $\alpha$ -pinene with acids at temperatures above  $-80^\circ \text{C}(\text{I})$ . We think that this is enough to rule out the existence of XII in any case formed by acid dimerization of  $\alpha$ -pinene. On the other hand if the bicyclic unit of the dimer(s) was XI the two monomeric units would be connected through secondary carbon atoms. In this case, the fragmentation of this bond would be highly improbable as the primary process and we would not have observed the high peak at  $m/e$  133.

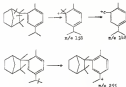
A probable mechanism for formation of fragment  $m/e$  69 from XIX is (XX).



### Mass spectrum of dehydrogenated mixture

A mixture of XVIIIa and XVIIIb was dehydrogenated with 5 per cent palladium on charcoal. The main characteristics of the mass spectrum of the dehydrogenation product are discussed in this section (Figure 7).

The peak at  $m/e$  133 disappeared and new peaks appeared at  $m/e$  143, 158 and  $m^+ - 15$ . The disappearance of  $m/e$  133 is explained by the fact that the bond connecting the two units is less easily broken because it is attached to an aromatic ring. On the other hand the bonds which are in "benzylic position" are more vulnerable, and the following fragmentation processes are very probable.



The  $m/e$  49 peak remains strong after the dehydrogenation indicating the presence of biopropyl units.

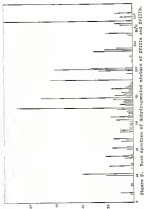
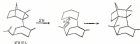


Figure 3. Mass spectrum of dehydrogenated alcohols at various temperatures and pressures.

An interesting feature of the spectrum is a very strong peak at  $m/e$  176 [base peak] which can be explained as the parent peak of product(s) formed by hydrogen disproportionation. The very strong peak at  $m/e$  176 indicates that this compound must possess exceptional stability. The only other peak generated from this molecular ion is  $m/e$  159 ( $176-17$ ). Such a compound must not have free isopropyl groups and the two ring system must be connected with more than one bridge [22]. The following rearrangement (probable under the reaction conditions) would lead to such a molecule.



Molecular models of this structure show that it is strain free. This would be the more reason for the great stability of the molecular ion.

#### NUCLEAR MAGNETIC RESONANCE

We have calculated the expected positions of the absorption maxima in the ultraviolet spectra of XVIIa

and XVIIb, by using Woodward's assumptions (45). In Table 18 we have tabulated the calculated and the experimental values for the two diast and also for the corresponding values for 2,4(5)-p-methylenes (XXII) and 2,8(9)-p-methylenes (XXIII), found in the literature (46). The calculated and the experimental values are in fair agreement.

TABLE 18  
Theoretical Absorption Values of  
Compounds XVIIa, XVIIb, XXII and XXIII

Compound	Calculated (in mμ)	Found (in mμ)
XVIIa	267	258 ( ± 10.000)
XVIIb	278	270 ( ± 20.000)
XXII	262	266 ( ± 15.043)
XXIII	272	275 ( ± 6.953)

#### Infrared Spectral Data

The infrared spectra of XVIIa and XVIIb are similar with the main difference being that XVIIa has an absorption corresponding to  $\text{C}=\text{CH}_2$ . The most characteristic infrared absorptions of the two compounds are given below:

Compound XVIIa:

885 and 815  $\text{cm}^{-1}(\text{a})$ : Pair of bands indicating



1385  $\text{cm}^{-1}(\text{a})$ :  $\text{C}=\text{CH}_2$

1376, 1345  $\text{cm}^{-1}(\text{a})$ : gem. disubstit

## Compound XVIIIb:

$770$  and  $810\text{ cm}^{-1}(\nu)$ : Pair of bands indicating  
 $1670\text{ cm}^{-1}(\nu)$  :  $\text{C}=\text{CH}_2$   
 $815\text{ cm}^{-1}(\nu)$  :  $\text{C}=\text{CH}_2$  (  $\beta$  CH out of plane)  
 $1370, 1380\text{ cm}^{-1}(\nu)$  : gem. dimethyl



No absorption was found corresponding to  $\alpha, \beta$ -disubstituted double bonds.

On the basis of the spectroscopic data discussed in this chapter, the following assignments must be ruled out as parts of the class XVIIIa and XVIIIb, for the reasons stated below:



It would give a strong peak at  $\nu/\text{cm}^{-1}(\text{R})$  because the isopropyl group is in the allylic position.



For the above reason, and also because there is no infrared absorption corresponding to  $\alpha, \beta$ -disubstituted double bond.

All structures with  
not conjugated  
double bonds.

They would not give absorption  
maxima above  $210\text{ m}\mu$ .

All structures with  
two conjugated bonds  
is a ring.

They would absorb at longer wave  
lengths ( $260-270\text{ m}\mu$ ).

### Triplet Acetylide Polymerization Products

The NMR spectra of both XVIIIa and XVIIIb were complicated as it would have been expected from segments with thirty two protons with very close chemical shifts. However, the study of the NMR data revealed valuable information supporting the proposed structures for these segments.

Segment XVIIIa (Figure 10) had one proton at 4.43 ppm indicating non-terminal (trisubstituted) double bond (4H<sup>a</sup>). The peaks from 4.50 to 5.30 ppm (12 protons) are assigned to the four methyl groups (8, 9, 10, 7')<sup>a</sup>. The peaks from 5.40 to 5.43 correspond to the methyl and methylene protons alpha to double bonds (5', 10', 3'), and to part of the proton of the methoxymethyl group. The peak at 6.75 is probably due to the proton at 1' position.

Segment XVIIIb (Figure 11) had two types of olefinic protons. One proton at 4.16 ppm (non terminal double bond), and two protons at 5.20 (terminal methylene). The peaks at 4.50 to 5.05 ppm corresponded to the twelve methyl protons at 8, 9, 10, and 7' carbon atoms.

<sup>a</sup>The numbering of carbon atoms is given in the following formula:



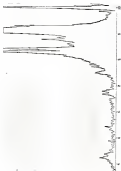


Figure 10. X-ray spectrum of radium ( $\gamma$  rays).



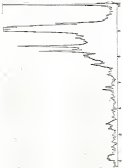


Figure 11. NMR spectrum of DVTB in  $CDCl_3$ .

The NMR spectrum of the hydrogenated diene had no vinyl peaks. There were two groups of peaks, one at 4.5 to 5.5 ppm corresponding to the vinyl proton and another at 1.5 to 2.5 ppm corresponding to the methylene and methine protons. A small peak at 7.5 ppm could be probably assigned to the bridgedhead hydrogen.

#### Mechanism of Polymerization of Diene

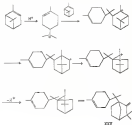
A possible mechanism accounting for the formation of diene XVIIIa and XVIIIb is the following:



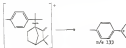
It is probable that steric reasons account for the fact that XVIIIa polymerized to give a syndiotactic ring instead of a second triallyl system.

The larger amounts of dimer XVIIIa formed can be explained by the fact that its olefin system is more substituted, and thus the molecule is energetically favored over XVIIIb.

The mass spectral data of XVIIIa and XVIIIb, discussed above, indicate that the dimers are composed of a norbornene and a bicyclic unit connected through at least one tertiary carbon atom. An alternative to the formation of each dimer is given in the following reaction series:



Further, structures like III are ruled out for two reasons. First, they cannot explain the positions of the absorption curves in the ultraviolet region. Second, their deprotonation reaction should give a very strong peak at  $m/e$  133 because of the direct formation of the stable  $p$ -quinodimethane.



## SYNTHESIS OF 3,3'-BIPHENYLENE

### General discussion of the reaction of benzene with alkaline silver salts of long alcohols

It has been reported that the carbon-carbon bond breaks homolytically when treated with alkaline silver salts (46). Brown and his collaborators (43 a,b) were the first to develop this reaction as a synthetic method for the coupling of alkyl groups. Thus, alcohols were hydrobromated by the usual methods (49) and the alkyl bromides formed in situ were oxidized with alkaline silver salts.



We thought that this reaction could be very useful for synthesizing olefinic terpenes of known structure. For this reason we decided to explore and develop it further.

### Evidence of the reaction

There is strong evidence in the literature for the free radical character of this reaction and of other similar reactions (32). It has been found (46b) that in presence of  $\text{OCl}_2$ , chlorinated products are formed, and also, that the reaction caused polymerization of styrene.

In addition, we have carried out the reaction in the presence of  $\text{BzOCH}_3$ . Brominated compounds were formed, and the formation of coupling products was suppressed. When we carried out the reaction in the presence of diethyl-piocyridimide, there was a rapid change in color from violet to yellow.

From the above data it is reasonable to adopt the following scheme:



The reaction is very slow when the allylthiuronium is treated with silver oxide in the absence of alkyl hydrides. The role of  $\text{OH}^{\bullet}$  in accelerating the oxidation is not yet clear. An explanation could be that the allylthiuronium coordinates with  $\text{OH}^{\bullet}$  and so, the 3-4 bonds become weaker and break easier. To test this assumption we treated allylthiuronium with silver oxide in the presence of other strong hydrogen donors, such as hydrazine and sodium ethoxide, but no reaction was noticed.

The by-product found, in the reaction mixture, in the form of sodium benzoate. It is probable that the driving

scope of the oxidation reaction is the energy of formation of the solvated borate ion. However, the details of the mechanism of the coupling reaction remain unknown.

#### Reaction with alkaline lead dioxide

During the course of this work we have investigated the possibility of using oxidizing agents other than silver oxide. Lead dioxide in alkaline solution gives similar yields, it is less expensive and it is easier to handle.

We have applied the same free radical tests for the oxidation with alkaline lead dioxide and we found that in this case, as in the case of silver oxide, intermediate radicals are involved. The fact that the oxidation of triphenylmethyl borane with both reagents gives the same isomeric products is exactly the same result indicates that both reactions involve the same reactive intermediates.

We have further, considered the possibility of rearrangements of the intermediate free radicals. Under the reaction conditions any skeletal rearrangement was found to be highly improbable. We have carried out the coupling of hydrobromated  $\beta$ -pinenes and have found that only the one expected dimer is formed. Also, tri-*n*-propylborane gives mainly *n*-decane (48%).

#### Oxidation of diolboranes

We have oriented the study and usefulness of the reaction by developing it as a new synthetic tool for the synthesis of tetrasubstituted 1,3-butanediols.

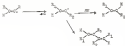
It was found that by treating vinyl benzenes with lead dioxide in alkaline solution there were formed 1,3-dienes in fair yields. The vinyl benzenes were formed in situ by saponifying disubstituted alkenes (48).



Trans dienes were formed as by-products.

The oxidation of vinyl benzenes with lead dioxide involves free vinyl radical intermediates. When the reaction was carried out in  $\text{BrCH}_2\text{CH}_3$  or  $\text{CCl}_4$ , brominated and chlorinated products were formed and the formation of dienes was suppressed.

This lead us to the study of the geometric stability of the vinyl radical (51). It was concluded that under the reaction conditions the vinyl radical has no geometric stability. The cis and trans forms are in rapid equilibrium and the products formed originate from the energetically favored trans form.





### Hydroboration and coupling of $\alpha$ -pinene

We have applied this reaction as a route to the synthesis of the isomers 3,3'-dipinenes. Then  $\alpha$ -pinene was hydrobored, and the hydroboration mixture was treated with  $\text{AgNO}_3$  and methanolic KOH, or with  $\text{FeO}_2$  and methanolic KOH. The reaction mixtures were analyzed by T.l.c. and the dieneic isomers were separated by preparative size and chromatography.

When starting with optically pure (+)- $\alpha$ -pinene there were observed three dieneic isomers XXVla, XXVIlb, XXVIlc, in the ratio of 1:1:0.87. When starting with pure (-)- $\alpha$ -pinene there were observed again three dieneic isomers XXVId, XXVIf, XXVIfb, with the same retention times and in the same ratio. The first two dieneic, in both cases, were isolated by v.p.d. The IR and NMR of XXVId and XXVIf and XXVIlb and XXVIfb were superimposable but the compounds had opposite optical rotations (Table II).

TABLE II  
Optical Rotation of Dipinenes

Starting Material	Dieneic	$[\alpha]_D^{25}$ in $\text{CHCl}_3$
(+)- $\alpha$ -pinene	XXVId	+32 <sup>a</sup>
	XXVIlb	+27 <sup>a</sup>
(-)- $\alpha$ -pinene	XXVId	+32 <sup>b</sup>
	XXVIfb	+25 <sup>b</sup>

It is therefore concluded that XVIIa, b and XVIIIa, b are enantiomers. Although we were not able to isolate and study XVIIIa, b, since they are formed in very small amounts, it would be safe to assume that these are the third separated enantiomeric pair.

From a partial cleavage of diphosphate that acted as starting material, three more dienes were observed, XIX, XX, and XXI, besides the XVI, XVII, and XVIII. The retention times of the six isomers, in three different columns, were in the following order:



The molecular weight of the dienes was found, by mass spectrometry, to be 774. The C, H analysis corresponded to  $\text{C}_{25}\text{H}_{36}$  (calculated: C, 87.96; H, 12.04. Found: C, 87.52; H, 12.53). They were viscous liquids which crystallized, when optically pure, to low melting solids [XVI m.p.  $53-5^{\circ}$  (pellets), XVII m.p.  $53-6^{\circ}$  (needles)]. The structural assignments for XIX and XXII were based on their NMR spectra. The spectrum of XIX was similar than that of XVII indicating that this isomer had higher symmetry. The spectrum of XXII showed fewer axial hydrogens. Therefore, XIX is the isomer with the larger number of equatorial methyls. The assignments of the methyl groups were made as follows ( $^{\circ}\text{C}$  values in ppm):

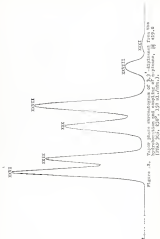


Figure 3. Total photo absorption of 3,3'-diplumet from the hydrolysis and coupling of diphenylamine, [H] 109.8 (1000  $\mu$ g, 600°, 1/2 d. film, J.

XXVI:  $\epsilon_D$  5.75,  $\epsilon_D$  5.85,  $\epsilon_{12}$  5.54 (axial),  $\epsilon_D^*$ ,  
 $\epsilon_D^*$ ,  $\epsilon_{12}^*$  as  $\epsilon_D$ ,  $\epsilon_D$ ,  $\epsilon_{12}$

XXVII:  $\epsilon_D$ ,  $\epsilon_D^*$  5.75,  $\epsilon_D$  5.85,  $\epsilon_{12}$  5.55 (axial),  
 $\epsilon_{12}^*$  5.55 (axial),  $\epsilon_D^*$  5.84.

They were based mostly on values found for a number of monoterpenes [35] with similar structures.

The mass spectral data, the relative boiling points, and refractive indices support the structural assignments. It has been observed that for a given pair of diastereoisomers, the thermodynamically more stable one will exhibit the more intense molecular ion peak (3). Thus, XVI is expected to be thermodynamically more stable than XVII because both  $\epsilon_{12}$  and  $\epsilon_{12}^*$  methyl groups are equatorial whereas in XVII, one is axial and one equatorial.

As expected, the molecular ion peak of XVI is more intense than that of XVII (200  $\frac{I}{I_{200}}$  is 4.9 for XVI and 2.6 for XVII).

On the other hand, the van der Waals rule predicts both among allylic systems, not differing with in double bond, the lower of highest orbital has highest boiling point and refractive index (34).

The results are what would have been predicted by the above rule (Table II). Instead of the boiling points, we reported the relative retention values of the diene, which were similar in three different chromatographic columns.

TABLE 12  
Relative Retention Values of Diastere

Diast	Relative Retention Values (in 25°C)	$\frac{d \log R}{d T}$	Substrate in 10 and 25° Positions
XXVI	1	1.4833	a, a
XXIX	1.07	1.4838	a, a
XXX	1.25	1.4865	a, a
XXVII	1.55	1.4850	a, a
XXVIII	1.59	—	a, a
XXXI	1.70	—	a, a

The following generalizations can be made:

1. The more axial acetyl groups (high anisotropy) the higher the boiling point.
2. The higher the symmetry (lower anisotropy) of the diast the higher the boiling point.

Further experiments directed toward confirmation of the above structural assignments involved treatment of the different isomers with Pt/C. It has been reported that by heating axial equibromanes with hydrogenation catalysts equilibration is achieved between axial and equatorial forms, and the final product is richer in the more stable isomer, the ratio depending upon the relative anisotropies of the two isomers (15). Thus, by heating for three days at 250° C., different diastere fractions with

of palladium on charcoal it was observed that compounds XXVI and XXIX did not show any change. On the other hand, the T.P.C. peaks corresponding to XXVII and XXX diminished and new peaks were observed in the region of the diastereoisot compounds. The small hump corresponding to XXVIII and XXXI disappeared after this treatment.

The volatile part of the reaction mixture from the oxidation of isopimaricacetylbenzene with  $\text{Ag}_2\text{O}$  was composed of unreacted isopimene and pinene. The formation of pinene is explained by hydrogen abstraction by the intermediate free radical from solvent molecules.

### Nomenclature

In Table 13 are given the structural formulas of the leucadiene di-pinanes. The specification of stereochemical configurations are according to the "sequence rule" (36). We have preferred the general term "di-pinane" because it indicates directly the ring system of the monomeric unit.

Another way to name these compounds could be based on the nomenclature of the leucadiene pinosapichols (37):



XXII, 4,4'-bis(2-methyl-2-propenyl)-2,2'-biphenyl;  
 XXIIIa, 1-isopropenyl-4-(2-methyl-2-propenyl)-2-phenyl;  
 XXIV, 4,4'-bis(isopropenyl)-2,2'-biphenyl, etc.

Table 15

Isomer 3,3'-Biphenyl

XXV, 2,2'-bis(2-methyl-2-propenyl)-3,3'-biphenyl

XXVI, 1-isopropenyl-4-(2-methyl-2-propenyl)-3-phenyl

XXV

XXVI



XXVII, 2,2'-bis(2-methyl-2-propenyl)-3,3'-biphenyl

XXVIII, 1-isopropenyl-4-(2-methyl-2-propenyl)-3-phenyl

XXVII

XXVIII



XXIX, 2,2'-bis(2-methyl-2-propenyl)-3,3'-biphenyl

XXX, 1-isopropenyl-4-(2-methyl-2-propenyl)-3-phenyl

XXIX

XXX

### Discussion

The transition in the  $\beta$ -pinene diastereoisomers can be rationalized as follows. If we start with (+)- $\alpha$ -pinene, this side  $H_2H_3$  is an anti- $\beta$ -homomethyl number and from the less hindered side to give XXXII (3a).



This is obtained by the axial attack to the free radical XXXII. The free radicals formed can be avoided from either side. Coupling of two radicals from side 1 gives isomer XXXIV. Coupling of one radical from side 1 and one from side 2 gives 'XXXIVa' which rearranges to the more stable conformer XXXIVb.



Similarly, when two radicals couple from side 2, XXXIIIa is formed.



By starting with (-)- $\alpha$ -pinene we get the corresponding enantiomers XXVII, XXVIII, XXIX.

If there are not geometric preferences in the manner of coupling of the free radicals the ratio of the three isomers would be XXVI:XXVII:XXVIII=1:1:1. By inspection of the molecular models it can be seen that the relative energies of the transition states corresponding to the formation of the three dimers are:



This explains the relative order of the observed ratio of products (1:1:0.87).

When starting with mixtures of (+) and (-)- $\alpha$ -pinene we observe the formation of isomers generated from the coupling of the two different radicals. There are XXX, XXX (and its enantiomer), and XXXI. Compounds XXX and XXXI possess planes of symmetry.

### Experimental Part<sup>1</sup>

#### Hydroboration and coupling of $\alpha$ -pinene

To 0.1 mole  $\alpha$ -pinene and 15 ml. 25%  $\text{NaBH}_4$  in diglyce-  
re at 0° C., was added slowly 0.1 mole  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ . The mixture  
was stirred for one hour at room temperature. Ten  
ml. of water was added to destroy the excess of hydride.

1

<sup>1</sup>See also several experimental parts pp. 31-32.

and, after cooling in an ice bath, were added 160 ml. 2N KOH in methanol, and slowly 45 ml. 3N  $\text{AsO}_3$ . The whole reaction was carried out under  $\text{N}_2$ , to avoid the formation of oxygenated products. After stirring for 3 hours at room temperature the mixture was filtered with suction. The precipitate was washed with 15 ml. acetone in small portions and 30 ml. pentane. To the combined filtrate and washings were added 100 ml. water and the two phases separated. The aqueous layer was extracted three times with 30 ml. pentane, and the combined pentane extracts were washed with water, dried over  $\text{CaH}_2$ , and the solvent evaporated to give a syrup containing 30-40% dienes, n-pinene and pinene.

Alternatively, to the hydroboration mixture were added 30 grams  $\text{FeO}_3$  and 120 ml. KOH and the whole was stirred overnight at room temperature. The reaction mixture was subjected as above. The same procedure was used for the coupling of hydroboration products.

#### Treatment of hydroboration products with $\text{As}_2\text{S}_3$ in the presence of $\text{CCl}_4$

To the hydroboration mixture were added 30 ml.  $\text{CCl}_4$ , 50 ml. 2N KOH and 11 ml. 3N  $\text{As}_2\text{S}_3$  and the mixture was stirred for 16 hours at room temperature. The reaction mixture was introduced into the mass spectrometer through a short column (3 ft., Carbowax 100). The mixture was

resolved into three broad peaks, but each peak corresponded to a group of unresolved peaks. The mass spectrum of the second peak had a molecular ion peak at  $m/e$  138 and another at  $m/e$  134 ( $M^+ - 4$ ) indicating the presence of  $C_{12}H_{17}OCl$ . The mass spectrum of the third peak had a molecular ion at  $m/e$  134 ( $C_{12}H_{17}OCl$ ). This last peak was isolated by preparative gas chromatography. The infrared spectrum indicated secondary alcohol.

#### Trimerization of polyunsaturated alkenes with $Ag^+$ in the presence of $NO_2^-$

The reaction was carried out as above with the exception that  $HgCl_2$  was used instead of  $CCl_4$  and the mixture was stirred for only one hour. The mixture was analyzed by r.p.g.c. (Carbowax 80B column). The main component was isolated by preparative gas chromatography. It precipitated silver bromide when treated with aqueous silver nitrate. When the reaction mixture was refluxed with silver nitrate, the bromide disappeared and a new peak appeared in the aprotic region.

#### Extrimerization and coupling of alkenes

To 0.12 moles of alkene and 10 ml.  $NaOH$  in dioxane, cooled to  $0^\circ C$ , were added 5 ml.  $BF_3 \cdot Et_2O$ . After stirring for 0.5 hour at  $0^\circ C$ , and 0.5 hour at room temperature the mixture was cooled in an ice-salt bath and there were added 15 g.  $PbO_2$  and 10 ml. 48 HBr. The mixture was stirred for 2 hours, filtered, and the precipitate was

washed with acetone and pentane. The combined filtrates were washed with dilute NaOH and water and dried over  $\text{Na}_2\text{SO}_4$ . The yield is almost 50-60%. The products were analyzed with a 10% Carbowax 80W column. They gave the expected IR, UV, NMR and mass spectra. By this method were prepared trans, trans-1,2,3,4-tetraethyltetrahydronaphthalene (XXIII) and tetrapropyltetrahydronaphthalene (XXIV). Hydrogenation and coupling of  $\beta$ -octyne gave trans isomeric dienes in the expected ratio of 1:1.

#### Spectroscopic Data on tetra-substituted tetrahydronaphthalenes

Compounds XXIII and XXIV were isolated by distillation with a spinning band column. The UV maxima had an absorption maximum at 230 m $\mu$ . The infrared spectra indicated monosubstituted. The mass spectrum of XXIII had a molecular ion peak at m/e 186 and another major heavy fragment at 137 ( $\text{C}^2\text{-CH}_2\text{CH}_3$ ). The mass spectrum of XXIV had a molecular ion peak at m/e 170 and other major heavy fragments m/e 123 ( $\text{C}^2\text{-CH}_2\text{CH}_3$ ) and 159 ( $\text{C}^2\text{-CH}_2\text{CH}_2\text{CH}_3$ ).



XXIII



XXIV

A first order analysis of the NMR spectra of XXIII and XXIII gave the following results ( $\tau$ -values in ppm):

- XXIII:  $a = 4.56$ ,  $b$  and  $b' = 7.67$  and  $7.68$ ,  $c$  and  $c' = 3.08$  and  $3.09$ ;  $J_{ab} = 6.7$  cps,  $J_{ab'} = 2.2$  cps,  $J_{bc} = 4.8$  cps; areas  $(a + a')/(b + b') = 1.14/1.04$ ,  $(b + b')/(c + c') = 1.14/1.04$ .
- XXIII:  $a = 4.58$ ,  $b$  and  $b' = 7.65$ ,  $c$  and  $c' = 3.47$ ,  $c$  and  $c' = 3.46$ ;  $J_{ab} = 7.0$  cps; areas  $(a + a')/(b + b') = 1.14/1.04$ ,  $(b + b')/(c + c') = 1.14/1.04$ .

The NMR data of XXIV are the following ( $\tau$  in ppm):



XXIV

$a, a' = 4.78$ ,  $b, b' = 7.59$ ,  $c = 3.47$ ,  $d = 3.05$ . The vinyl protons have a large coupling ( $J_{bc} = 7$  cps) and a small coupling ( $J_{bd} = 1.1$  cps). Areas  $(a + a')/(b + b') = 1.14/1.04$ ,  $(b + b')/(c + c') = 1.14/1.04$ .

Compound XXIV has formed as a by-product of the hydrogenation and coupling of 3-octenes. Its infrared spectrum superimposed on the spectrum of trans-3-octene, found in the literature (23).



## ABSTRACT

In the present work a systematic study has been made of the dissociation of  $\alpha$ -pinene with boron trifluoride gas or its coordination compounds with ethers, amines and phosphines. The reaction of  $\alpha$ -pinene with boron trifluoride as the etherates gives very complex diastereomixtures. The reaction of  $\alpha$ -pinene with  $\text{BF}_3 \cdot \text{P}(\text{C}_2\text{H}_5)_2$  gives a diastereomixture with only two main components. These two diastereomers were isolated by preparative vapor phase chromatography. Their structural assignments were based on a detailed study of their mass spectra, and were supported by their infrared, ultraviolet and nuclear magnetic resonance spectra, and the nature of their hydrogenation, dehydrogenation and ozonolysis products. A mechanism is proposed accounting for their formation.

The oxidation of bornenes with lead oxide and silver oxide was extensively studied and it was developed as a route for the synthesis of diastereomeric diastereomers of definitely known structure. By this method were prepared and studied the six isomers  $\beta,\beta'$ -dipinanes. The stereochemistry of the intermediate bicyclic peroxide radical was discussed in detail.

The oxidation with lead dioxide or silver oxide was extended to vinylbenzene. This is a new accessible route to tetrasubstituted trans, trans-dibenzenes. The oxidation of vinylbenzene was used for the generation and study of geminate stability of the intermediate vinyl radicals. It was found that the cis-trans equilibration of the intermediate vinyl radicals is more rapid than their coupling or hydrogen abstraction reactions. Thus, the vinyl radical has no geminate stability under the reaction conditions.



# REFERENCES

1. Hargrove, J. L., *The Terpenes*, Vol. II, 2d Ed. (1949) pp. 109-130, The University Press, Cambridge.
2. a. Benson, F. L., Carbonium Ion rearrangements in bridged bicyclic systems, 185-9. in *Molecular rearrangements*, 2d Ed. F. L. Ingley, Interscience Publishers, New York, 1963. b. Christensen, A. J., *Synthetic displacement reactions*, McGraw Hill Co., New York (1962).
3. Deville, E., *Annales de Chimie et de Physique* 33, 39 (1842).
4. a. Kostikov, I. L. and Sapozhnik, S., *Bull. Acad. Chim. France* 37, 933-934 (1945); b. *Ibid.* 37, 1245-46 (1945).
5. DeLong, E., *Chem. et Ind.* 37, 43-44 (1934).
6. DeLong, E., *Deutsche. Vol. 4, Forts. Ind.* 333, (No 1), 49-53.
7. a. Ritter, J. J. and Sharafkin, J. G., *J. Am. Chem. Soc.* 62, 1504-1509 (1940); b. *Ibid.* 66, 1993-19 (1943).
8. Roberts, W. J. and Day, A. E., *J. Am. Chem. Soc.* 72, 1266-70 (1950).

9. Baker, M. A., Smart, A. F. and Gider, V. E., Fifth Regional Meeting, Delaware Valley Section, A. C. S., Philadelphia, Pa. (Feb. 1958).
10. Baker, G. E. and Eckert, E. E., *Seitman-Greifman Regional Meeting of A. C. S., Memphis, Tenn.* (Dec., 1963).
11. For an introduction to non classical ions see, Bartlett, P. F., *Non Classical Ions - Reprints and Commentary*, P. A. Benjamin Inc., New York (1965).
12. a. Ingold, C. K., *Ann. Reports* 35, 397 (1938);  
b. Bartlett, P. F., de Scales, E. and Wilson, P. L., *J. Chem. Soc.*, 1939, 1159; c. Winstein, S. and Felton, D., *J. Am. Chem. Soc.*, 73, 1136-60 (1951).
13. a. Le Hy, S., *Compt. rend.*, 251, 1326 (1960); b. Goering, H. S. and Sloan, R. F., *J. Am. Chem. Soc.*, 83, 1397-1401 (1961); c. *Ibid.*, 83, 1894-99 (1961); d. Winstein, S. and Carter, F., *Ibid.*, 83, 5483-6 (1961); e. Bartlett, P. F. and Bush, G., *J. Am. Chem. Soc.*, 83, 1395 (1961).
14. Kricheldorf, H. F., Korman, L. E. and Goering, H. F., *J. Am. Chem. Soc.*, 82, 5366-69 (1960).
15. Kricheldorf, H. F. and Fargnoli, M. E., *J. Org. Chem.*, 29, 1945-196 (1964).
16. Brodie and Humphrey, *J. Am. Chem. Soc.*, 82, 6211-16 (1960).
17. Deane, R., *Science et Ind.*, 27, 423-48 (1952).

18. Beliquette, J., Ann. Chim. Appliquee, 22, 245-24 (1898); C. A. 22, 7082a.
19. Dupont, G., Delon, P. and Thuet, G., Bull. Soc. Chim. France, [3], 2, 431-2 (1941).
20. Korotkov, K. V. and Eliseev, P. T., Khimich. Sost. Akad. Nauk. SSSR, 1-2-2, Inst. Khim. 2, 129-5 (1957); C. A. 22, 14473d.
21. Hercules Powder Co., U. S. 2,178,349 (1937); C. A. 12, 1296 (1948).
22. Dupont, G. and Giffard, Bull. Soc. Chim. France, [4], 2, 1379-80 (1931).
23. Seydel, J., Ann. Chem. Soc. 21, 2133-75 (1949).
24. Hercules Powder Co., U. S. 2,497,746 (1954); Chem. Abstr. 1955, 1, 4361.
25. Salomon, J., Bull. Soc. Chim. France, [4], 21, 54-6 (1937).
26. Salomon, J., Salomon, J. and Sauer, E., Bull. Soc. Chim. France 27, 546-56 (1933).
27. Doong, G. C., Unpublished data.
28. Gehring - Kohlborn, A. G., Brit. 375,345 (1931); Chem. Abstr. 1932, 2629.
29. a. Arshonilov, V. I., U. S. P. 2,48,399 (1949); C. A. 42, 3775; b. Stempelov, E., et al., Pol. 22, 127 (1959); C. A. 23, 652d.
30. Lombard, E. and Kover, A., Bull. Soc. Chim. France, 122, 1415-9.

31. Nagai, K., *Bull. Chem. Sect. Univ. J.* 41 (1968).
32. Nagai, K., *Bull. Chem. Sec. Japan* 32, 1871-2 (1959).
33. Lachowik, *Comp. rend.*, 162, 533 (1886).
34. For a general review on Lewis catalysis see "Organal -Catalysis and Related Functions," Eick, R. A., Ed., Vol. I, Interscience Pub. (1963).
35. Eick, R. A. and Young, G. G., Unpublished work.
36. Brown, R. G. and Adams, R. N., *J. Am. Chem. Soc.* 62, 2527 (1940).
37. See references 34 pp. 82, 225-26, 374-6.
38. a. Evans, A. G., Newman, G. F. and Polanyi, M., *Nature* 135, 34 (1944); b. Evans, A. G. and Polanyi, M., *J. Chem. Soc.*, 252 (1947); Fleisch, F. G., Polanyi, M. and Skinner, E. A., *ibid.*, 257 (1947).
39. Clark, L., in *Cellulose Polymerization and Related Compounds*, From. Conf. Univ. Coll. North Staffordshire, Eng. (1958), pp. 99-108; G. A. 42, 3345 b.
40. Say, R. E., Private communication.
41. a. Linwood, R. F. et al., *J. Chem. Soc.* 1120 (1940); b. Zelinsky and Pavlov, *Russ. J.*, 1820 (1933).
42. Zelinsky et al., *Annalen*, 476, 60 (1935).
43. Schage, E. and Van Ormon, E., *Acta. Chem. Scand.* 12, 3023-35 (1958).
44. Thomas, A. P. and Williams, M., *Nature*, 62, 973 (1948).
45. Woodward, R. B., *J. Am. Chem. Soc.* 62, 72 (1940).

44. O'Connor, T. E. and Goldblatt, L. A., *Anal. Chemistry* 35, 1702 (1964).
45. Jackson, L. R., *Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press (1959).
46. a. Lippert, R. F., *Chem. Revs.* 55, 959 (1955);  
 b. Brown, E. G., Seibert, E. G. and Snyder, G. H.,  
*J. Am. Chem. Soc.* 83, 1001 (1961); c. Brown, E. G.  
 and Snyder, G. H., *ibid.*, 83, 1006 (1961).
47. Brown, E. G., Ephraïmowicz, F. A. Benjamin Inc.,  
 New York, 1962; see also Zweifel, G. and Brown,  
 E. G., *Epoxidation of Alkenes, Alkynes and Isoprenes*  
*via Epichlorohydrin*, in *Organic Reactions* Vol. 13, A.  
 C. Cross Ed., J. Wiley and Sons Inc., New York, 1963.
48. Weiss, F., Ed., *Chemokristalle Chemistry*, Reinhold  
 Publishing Corp., New York, 1960.
49. Butler, G. B. and Steninger, A., Unpublished  
 results.
50. Zweifel, G. and Brown, E. G., *J. Am. Chem. Soc.* 86,  
 193 (1964).
51. Dickinson, L., Rjersdal, G., Williams, E. H.,  
*Structure Elucidation of Natural Products by Mass  
 Spectrometry*, Vol. II (Oxford-New), 1966, p. 142-4.
52. Allinger, N. L., *J. Am. Chem. Soc.* 79, 7943 (1957).
53. e.g., Allinger, N. L. and Fu, Mibao, *J. Org. Chem.*  
27, 3419 (1962).

96. For the "sequence rule" for specifying absolute configuration see Conn. L. H., Ingold, C. K. and Prelog, V. *Experientia* 11, 81 (1955).
97. Schick, E., *Ber.* 81, 300 (1947).
98. Saunders, E. S., Bruttain, E. E. and Jones, P. S., *J. Chem. Phys.* 11, 116 (1943).

## BIOGRAPHICAL SKETCH

Alexis G. Chassikopoulou was born on March 20, 1935, in Athens, Greece. In December, 1958, he was graduated from the Chemistry Department of the School of Physics and Mathematics of the University of Athens, with the equivalent of the degree of Bachelor of Science in Chemistry.

After working for two years in the Greek Army, he was employed by Abbott Laboratories International. From September 1962, to August, 1963, he worked as Research Assistant in the University of Athens and Research Associate in the Technical University of Athens. He entered the Graduate School of the University of Florida in September, 1963. During his graduate study he worked as Teaching and Research Assistant and research associate.

Alexis G. Chassikopoulou is married to the former Lou Dornidas and is the father of one daughter, Maria. He is a member of the Union of Greek Chemists and of the American Chemical Society.

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as partial fulfillment of the requirements for the degree  
of Doctor of Philosophy.

August 13, 1968.

E. Ruffin Jones  
Dean, College of Arts and Sciences

\_\_\_\_\_  
Dean, Graduate School

Supervisory Committee:

B. B. Bull  
Chairman

Blair T. Brown

J. R. Thompson

G. E. H. Smith  
W. L. Smith